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## Atomic relaxations around vacancy clusters in molybdenum and their effects on trapped-positron lifetime

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The relaxations of first- and second-nearest-neighbor shells of atoms around a monovacancy and around voids corresponding to the removal of 9, 15, 27, and 51 atoms in molybdenum have been calculated by minimizing the total energies with respect to atomic displacements. The energies are obtained by using the tight-binding scheme within the moments and continued-fraction formulation. The sign of the atomic displacements (inward or outward) of both the nearest and next-nearest neighbors varies with the size of the void. In addition, the displacements exhibit oscillations as a function of void size and do not appear to converge to atomic relaxations characteristic on surfaces even for the largest void studied. The relaxation of the first-nearest neighbor has a significant effect on the lifetime of positrons trapped in monovacancies, bringing theory to much better agreement with experiment. This effect, however, diminishes and becomes insignificant as voids grow in size.

### I. INTRODUCTION

The irradiation of materials with high-energy electrons and ions creates a cascade of vacancies. At elevated temperatures, these vacancies may migrate and cluster to form voids. It is of both fundamental and technological importance to characterize the structure and size of these voids at submicroscopic stages. The electronic structure of the materials can be exploited for this purpose. It is clear that as a void begins to grow, a stage must come when it approximates an internal planar surface. The electronic properties, which are expected to be sensitive to the void size, would cease to provide useful structural information when this limit is reached.

In this paper, we present theoretical results on different electronic and lattice properties as a function of void size in molybdenum. These include atomic relaxations around voids, electron and positron charge distribution, and the positron annihilation rate. It is normally expected that atoms around a monovacancy would relax inward. However, it is not clear how these relaxations proceed as vacancies cluster to form voids. Clearly, when voids become infinitely large, they would represent internal planar surfaces. The relaxation of the nearest-neighbor shell of atoms (i.e., atoms nearest to the void center) around the void should then be very close to that seen by the surface layer atoms. How big does a void have to be for this limit to be reached? Do the atomic relaxations approach the surface limit monotonically as the voids grow in size? The displacement of atoms causes a further perturbation of the host electron densi-

ties. Since positrons are normally trapped by vacancy-like defects, and the lifetime of the trapped positrons depends on the electron densities around the trap, it is expected that atomic relaxations would also influence the positron lifetime. It is, then, of interest to know how the dependencies of positron lifetimes change with atomic relaxations around differing void sizes. The evolution of the surface characteristics as voids grow in size can be studied in a variety of ways. It is expected that the electron charge-density distribution and positron lifetime would approach the surface values just as the atomic relaxations around large voids do. What is not known is whether steady values for all of these properties are achieved for the same size of void.

This paper addresses the above questions. In Sec. II, we outline our theoretical methods. Section III contains the results and discussions. A brief summary of our conclusions are given in Sec. IV.

### II. THEORETICAL METHODS

The calculations involve two steps: the relaxation of nearest-neighbor (NN) and next-nearest-neighbor (NNN) atoms with respect to the center of the void and the computation of the positron annihilation characteristics (binding energy and lifetime) in voids in both unrelaxed and relaxed environments.

Relaxation studies require total-energy calculations as the atoms in the defect region move to their equilibrium values. Since we are interested in voids having up to 51 vacancies, even if one confined the atomic relaxation to innermost and next-innermost atoms, the perturbed re-

gion would include a few hundred atoms. An *ab initio* energy calculation<sup>1</sup> for such large systems is out of reach with present computational resources. In this work we study the energy changes using a simplified semiempirical tight-binding approach.<sup>2</sup> The total energy of the system<sup>3</sup> is expressed as a sum of the electronic term  $E_e$  and a semiempirical repulsive term  $E_R$ ,

$$E = E_e + E_R . \quad (1)$$

The electronic term  $E_e$  represents the energy gained

$$E_{\text{cor}} = -45U^2 \int_{E_F}^{\infty} \int_{E_F}^{\infty} \int_{-\infty}^{E_F} \int_{-\infty}^{E_F} \frac{n_i(E_1)n_i(E_2)n_i(E_3)n_i(E_4)}{E_1 + E_2 - E_3 - E_4} dE_1 dE_2 dE_3 dE_4 . \quad (3)$$

Here  $i$  is the site index,  $n_i(E)$  is the local  $d$  density of states at the site  $i$ ,  $E_a$  is the mean position of the  $d$  band at the site  $i$  determined so as to preserve local charge neutrality at the  $i$ th site, and  $E_F$  is the Fermi energy. The correlation contribution representing on-site correlation energy is based on a simplified Hubbard model with  $U$  as the average Coulomb integral.<sup>3</sup> For Mo<sup>4</sup>,  $U$  is 2 eV.

The repulsive term  $E_R$  includes contributions from the core-core repulsion and is taken in the Born-Mayer form

$$E_R = \frac{1}{2} A \sum_{i,j} \exp(-pR_{ij}/R_0) . \quad (4)$$

Here  $A$  and  $p$  are constants determined from the bulk equilibrium distance, cohesive energy, and the bulk modulus.

The remaining input for the energy calculation is the local density of states  $n(E)$  which is evaluated using the moment technique.<sup>2</sup> We construct the density of states from its moments through the continued fraction

$$n(E) = -\frac{1}{\pi} \lim_{\epsilon \rightarrow 0} \text{Im} G(E + i\epsilon) , \quad (5)$$

$$G(Z) = \frac{1}{Z - a_1 - \frac{b_1}{Z - a_2 - \frac{b_2}{Z - a_3 - \frac{b_3}{\ddots}}}}$$

where  $G(Z)$  is the resolvent,  $Z = E + i\epsilon$  is the complex energy, and  $a_i$  and  $b_i$  are the continued-fraction coefficients which are functions of moments of the density of states. In all our studies, only the first four moments or the first two sets of coefficients  $a_i, b_i$  were calculated for each site. The continued fraction was calculated by putting the remaining coefficients the same as that in the pure crystal. This is reasonable, as the higher  $a_i, b_i$  sense the effect of distant region which is the same in pure crystalline or defect case. All the calculations were carried out within the tight-binding framework, assuming an orthonormal set of tight-binding  $d$  states,  $|i, \lambda\rangle$ , where  $i$  is the site index and  $\lambda$  is the orbital index. The moments  $\mu_n$  can be expressed as<sup>2</sup>

when the discrete levels of atoms overlap to form the band. Since the main source of electronic bonding in transition metals like Mo lies in the  $d$  band,  $E_e$  can be expressed as a sum of the on-site  $d$  band energy,  $E_B$  and correlation energy,  $E_{\text{corr}}$ . These terms are expressed as

$$E_B = - \int_{-\infty}^{E_F} (E - E_a) n_i(E) dE , \quad (2)$$

and

$$\mu_n = \frac{1}{N} \sum_{i,j} \langle i, \lambda | H | j, \mu \rangle \langle j, \mu | H \cdots H | i, \lambda \rangle . \quad (6)$$

The Hamiltonian matrix elements  $\langle i, \lambda | H | j, \mu \rangle$  are written in terms of the  $d$ -hopping integrals  $dd\sigma$ ,  $dd\pi$ , and  $dd\delta$ , and these depend on the separation between sites  $i$  and  $j$ . For Mo, the values

$$\begin{aligned} E(dd\sigma) &= -0.0936 \text{ Ry} , \\ E(dd\pi) &= 0.0517 \text{ Ry} , \\ E(dd\delta) &= 0.0 , \end{aligned} \quad (7)$$

corresponding to the bulk equilibrium distance give a good description of bulk band structure.<sup>4</sup> Further, the hopping integrals were assumed to vary with distance<sup>5</sup> as

$$E(dd\lambda(R)) = E(dd\lambda(R_0)) \exp \left[ \frac{-q(R - R_0)}{R_0} \right] , \quad (8)$$

where  $\lambda = \sigma, \pi, \delta$  and  $R_0$  is the bulk equilibrium distance.

The value of  $q$  was chosen to be 3 as suggested by our earlier *ab initio* studies.<sup>5</sup> The constants  $A$  and  $p$  entering the repulsive contribution were taken as 1676.2 Ry and 11.3, respectively. This choice leads to values of 8.0 and 26.4 eV for the cohesive energy and compressibility of bulk Mo, respectively, which compare very well with the corresponding experimental values of 6.8 and 26.4 eV.

The calculations of positron annihilation characteristics with the unrelaxed and relaxed environments of the voids have been done using two different procedures. The first one is based on the simple jellium model<sup>6</sup> while in the second method the discrete nature of the ions is included. In the jellium model a void is modeled by creating a hole of radius  $R$  in the positively charged background,

$$n_{\text{ext}}(\mathbf{r}) = n_0(\mathbf{r} - \mathbf{R}) . \quad (9)$$

$n_0$  is the constant density of the positive charge background compensated by an equal density of electrons. We have assumed, for our calculation of  $n_0$ , one electron per Mo atom. The radius of the void is given by

$$R = R_{\text{WS}} N_v^{1/3} , \quad (10)$$

where  $R_{ws}$  is the radius of the Wigner-Seitz sphere and  $N_v$  is the number of vacancies forming the void. As the atoms relax around the void,  $R$  is changed to model the new environment. For atoms relaxing inward,  $R$  in Eq. (9) is reduced from the unrelaxed value by the same percentage amount calculated through our tight-binding energy-minimization procedure. The reverse is true when atoms relax outward. Only the relaxations of the first-nearest neighbor, with respect to the center of the void, are considered in this calculation.

Starting with Eq. (9) as the external perturbation, the electron charge densities around the void are calculated self-consistently using the density-functional method. The positron wave function  $\psi_+$  and the binding energy  $E_b$  are calculated by solving the Schrödinger equation for the positron, namely,

$$[-\nabla^2 + V_+(\mathbf{r})]\psi_+(\mathbf{r}) = -E_b\psi_+(\mathbf{r}). \quad (11)$$

The potential acting upon the positron,  $V_+(\mathbf{r})$ , can be written within the pseudopotential picture<sup>7</sup> as

$$V_+(\mathbf{r}) = -\phi(\mathbf{r}) + V_{\text{corr}}(n_-(\mathbf{r})) - V_{\text{corr}}(n_0) - V_0\theta(\mathbf{R}-\mathbf{r}). \quad (12)$$

$\phi(\mathbf{r})$  is the electrostatic potential of the electron due to the perturbation and  $V_{\text{corr}}$  is the positron-electron correlation potential<sup>8</sup> evaluated in the local-density approximation.  $n_-(\mathbf{r})$  is the self-consistent electron density and  $V_0$  is the kinetic energy of the positron in perfect Mo which is taken to be 5.88 eV.<sup>9</sup> Since there is only one positron at any given time in the lattice, only the 1s state of the trapped positron is calculated.

The positron annihilation rate is calculated from the positron and electron density distribution using the local-density approximation:<sup>10</sup>

$$\lambda = \int d^3r n_+(\mathbf{r})\Gamma(n_-(\mathbf{r})), \quad (13)$$

$n_+(\mathbf{r}) = |\psi_+(\mathbf{r})|^2$  is the positron density distribution function and  $\Gamma$  is the local annihilation rate and is a functional of  $n_-(\mathbf{r})$ . It is conventional<sup>6,9</sup> to express  $\Gamma$  as a sum of two contributions originating from positrons annihilating with valence electrons  $\Gamma_v(n_v(\mathbf{r}))$ , and core electrons  $\Gamma_c(n_c(\mathbf{r}))$ :

$$\Gamma(n_-(\mathbf{r})) = \Gamma_v(n_v(\mathbf{r})) + \Gamma_c(n_c(\mathbf{r})). \quad (14)$$

$\Gamma_v$  is approximated by the Brandt-Reinheimer formula,<sup>10</sup> whereas  $\Gamma_c$  is obtained empirically by fitting the calculated positron lifetime in the perfect host with experiment.<sup>11</sup>

This method does not take into account the discrete nature of the ionic positions in a solid. An alternate procedure<sup>9</sup> is to treat the ionic positions as they appear in an imperfect solid. The positron energies and wave functions are calculated by solving a three-dimensional Schrödinger equation. The charge density  $n_-(\mathbf{r})$  and the Coulomb potential  $V_{\text{Coul}}(\mathbf{r})$  are approximated by superimposing atomic charge densities:

$$n_-(\mathbf{r}) = \sum_i n_{\text{at}}(|\mathbf{r} - \mathbf{R}_i|), \quad (15)$$

$$V_{\text{Coul}}(\mathbf{r}) = \sum_i V_{\text{at}}(|\mathbf{r} - \mathbf{R}_i|),$$

where  $\mathbf{R}_i$  runs over atomic positions, and  $n_{\text{at}}$  and  $V_{\text{at}}$  are the atomic electron density and Coulomb potential, respectively. In addition, the total potential contains the electron-positron correlation potential for which a local-density approximation is used. The solution of the three-dimensional Schrödinger equation gives the energy eigenvalue and the wave function for the positron. From the wave function the positron annihilation rate is calculated using the local approximation

$$\lambda = \int d\mathbf{r} |\psi_+(\mathbf{r})|^2 \times [\Gamma_v(n_v(\mathbf{r})) + \Gamma_c(n_c(\mathbf{r})) + \Gamma_d(n_d(\mathbf{r}))], \quad (16)$$

where the 4d-level electron distribution  $n_d$  is now treated separately from the rest of the core electron density  $n_c$ .  $\Gamma_v$  is approximated by the Brandt-Reinheimer formula as before. For  $\Gamma_c$  and  $\Gamma_d$  the independent particle formula with constant enhancement factors  $\gamma_c$  and  $\gamma_d$  is used,

$$\Gamma_c(n_c) = \pi r_0^2 c n_c \gamma_c, \quad \Gamma_d(n_d) = \pi r_0^2 c n_d \gamma_d, \quad (17)$$

where  $r_0$  is the classical electron radius and  $c$  is the velocity of light. For the tightly bound core electrons we use the value  $\gamma_c = 1.5$  and for molybdenum the value  $\gamma_d = 2.20$  reproduces the experimental positron bulk lifetime of 120 ps. The comparison of the results of the two methods used will show that the dependence of calculated lifetimes on the choice of theoretical methods is not very large.

### III. RESULTS AND DISCUSSIONS

The results of the relaxation of first- and second-nearest-neighbor atoms located from the center of the monovacancy and voids (corresponding to the removal of 9, 15, 27, and 51 atoms) are plotted in Fig. 1. The negative (positive) relaxations mean that the atoms relax inward (outward) with respect to the void center. Both the first- and second-nearest-neighbors exhibit oscillatory behavior as a function of void size. Similar oscillatory behavior of relaxations of inner layers from surfaces has recently been reported.<sup>12</sup> Except for small voids (vacancy and nine-atom void) where the displacements of the first two nearest neighbors are opposite in sign, the atoms relax outward, thus reducing the interlayer distance. Although these displacements have not reached a steady value even for a 51-atom void, it is quite apparent that the relaxations around larger voids would have the same sign as that for the largest void calculated here. This observation is in agreement with relaxations of the surface layers studied recently using tight-binding and linear augmented plane-wave techniques<sup>13</sup> and experiment.<sup>14</sup>

Relaxations of atoms around monovacancies in Mo have been carried out by several investigators in the past. Using pair potentials, Ypma and Caspers<sup>15</sup> calcu-

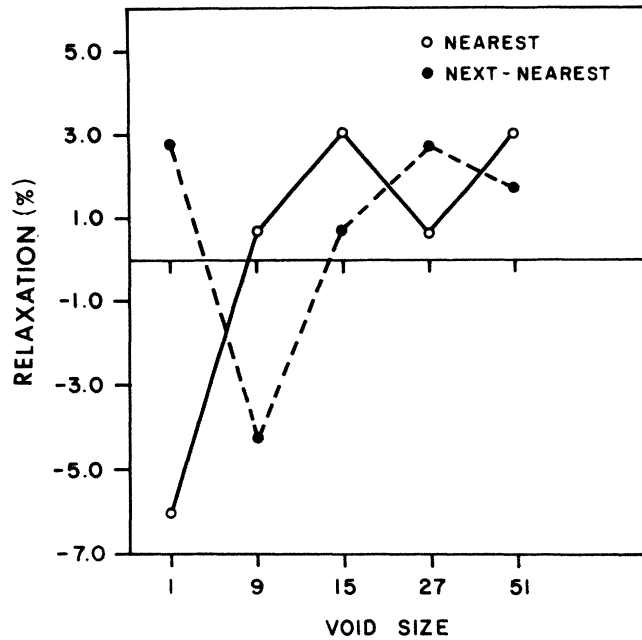


FIG. 1. Atomic relaxations of the first two nearest neighbors closest to the center of monovacancies and 9-, 15-, 27-, and 51-atom voids in Mo obtained from tight-binding calculations are presented as percent changes with respect to their unrelaxed distances.

lated the relaxation of the first-NN atoms around a vacancy to be  $-3\%$  (percent displacement refers to the unrelaxed distance). Mathai and Bacon,<sup>16</sup> using the  $N$ -body potentials of Finnis and Sinclair,<sup>17</sup> have carried out molecular-dynamics studies of atomic relaxations around vacancies and at surfaces of transition metals. Their results of an inward  $0.8\%$  relaxation of the first-nearest-neighbor atom around vacancies in Mo is much smaller

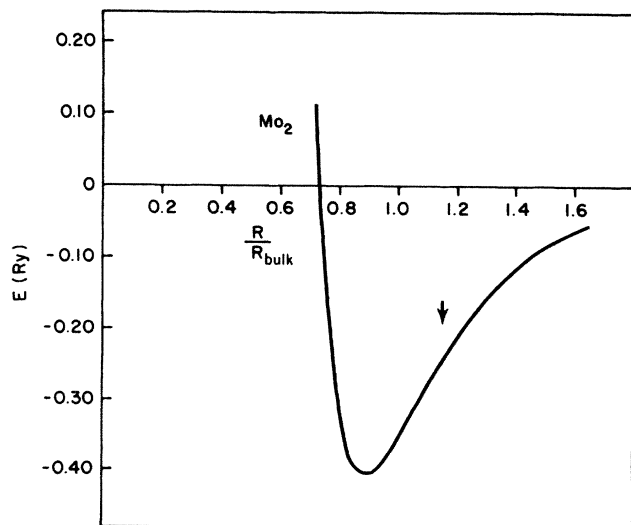


FIG. 2. Pair-interaction potentials of a Mo dimer. The arrow indicates the interatomic distance.

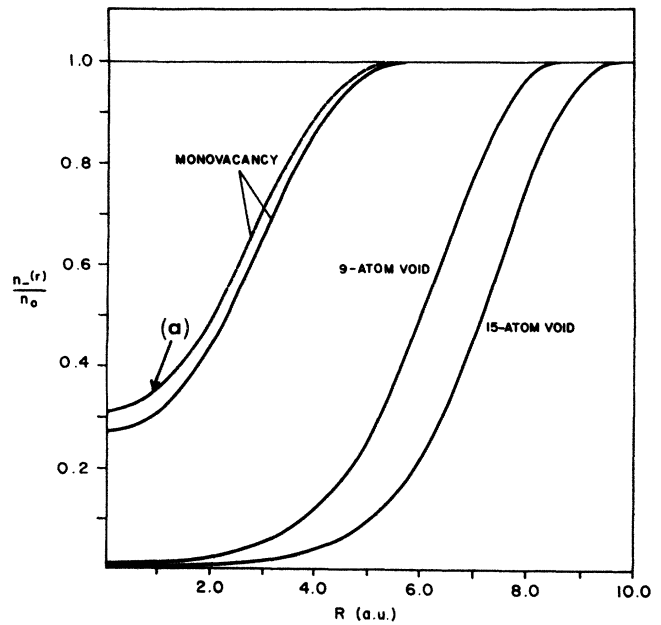


FIG. 3. Electron-charge-density distribution (normalized to the ambient value) around a monovacancy and 9- and 15-atom voids calculated in the jellium model. The curve (a) represents the effect of the nearest-neighbor relaxation.

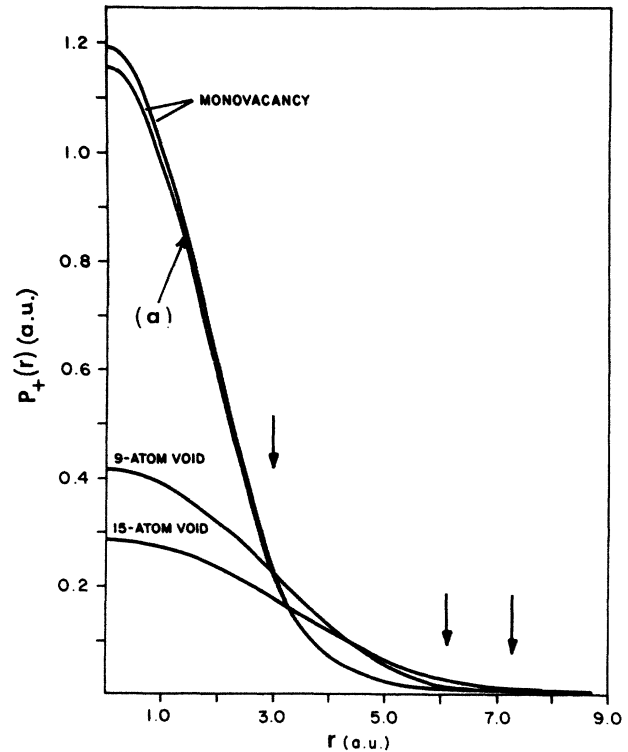


FIG. 4. Radial distribution  $P_+(r)$  of the positron wave function [ $\psi_+(r) = (1/\sqrt{4\pi})P_+(r)r$ ] around a monovacancy and 9- and 15-atom voids calculated in the jellium model. The curve (a) represents the effect of the nearest-neighbor relaxation. The arrows indicate the respective radii of the vacancy complexes.

TABLE I. Positron lifetimes and binding energies (measured with respect to the vacuum) in vacancy clusters of Mo using jellium model.

Void size	Binding energy (eV)	Lifetime (ps)
1 (unrelaxed)	1.02	194
1 (relaxed)	0.93	181
9 (unrelaxed)	5.28	400
15 (unrelaxed)	5.86	438
27 (unrelaxed)	6.41	458

than that of Ypma and Caspers's<sup>15</sup> and present results. These authors<sup>16</sup> also calculate an inward relaxation of 0.6% of the second-NN atoms which is qualitatively different from our results in Fig. 1. It will be shown later that a much larger relaxation (than discussed above) of first-NN atoms around vacancies is needed to explain the positron annihilation experiments.

The relative variations in the sign of the displacements of the first NN atoms can be understood in terms of a simple pair-ion interaction. We plot in Fig. 2 the pair potential of a Mo<sub>2</sub> dimer calculated using the tight-binding method outlined in the previous section. We first concentrate on the relaxation around the monovacancy. The location corresponding to the interatomic distance is indicated by an arrow in Fig. 2. At this distance, the atoms lie in the attractive region of the potential. Consequently, a decrease in the interatomic distance resulting from an inward relaxation of the first-NN shell gives rise to a gain in the pair-interaction energy. It should be pointed out that as the first-nearest neighbors relax inward, the distance between the first- and second-nearest neighbor would increase. This, in turn, would cost additional pair-interaction energy. It is the relative strength of these two energies that ultimately determines the magnitude and sign of the relaxations. For voids of nine atoms and larger, the interatomic distances between the first-nearest neighbors lie in the flat region of the pair potential in Fig. 2. Thus, no energy can be gained by an inward relaxation. On the contrary, energy is gained by reducing the interlayer distance in large voids. Another interesting feature, somewhat unrelated to the present discussion, is that the equilibrium dimer distance is about 11% less than the bulk value. This result is consistent with the recent observation<sup>18</sup>

that the interatomic distance in clusters of metal atoms increase with cluster size and approach the bulk value when clusters contain in excess of 50 atoms.

In Figs. 3 and 4, we plot the positron and electron density distribution around a monovacancy and 9- and 15-atom voids calculated in the jellium model. The effect of an increasingly attractive potential in larger voids is to localize the positron distribution function even more within the void, as can be seen from Fig. 3. This localization in positron density in regions of low electron density is responsible for the sharp increase in positron lifetime as voids get larger. In Figs. 3 and 4, we also show the comparison of positron and electron densities between the relaxed and unrelaxed monovacancies. Note that the inward relaxation of neighboring atoms causes the electron (positron) density to rise (fall) inside the hole. Consequently, the positron lifetime in relaxed vacancies decrease over that in unrelaxed environment. The electron density distribution in vacancy complexes shown in Fig. 3 illustrate the role of increasing repulsive term as voids grow.

In Tables I and II, we compare the positron lifetimes for various voids for relaxed and unrelaxed configurations using the jellium and the noninteracting discrete lattice model, respectively. While the trends in both the tables are similar, there are some quantitative differences. While the jellium model<sup>6</sup> incorporates the perturbation caused by the void on the ambient electron distribution self-consistently, it ignores the discrete lattice structure around the void. The discrete lattice model,<sup>9</sup> on the contrary, neglects the self-consistency problem associated with charge perturbation. Thus, the quantitative differences in the results between Tables I and II are indicative of the limitations of the theoretical models.

The effect of lattice relaxation on positron lifetimes in monovacancies is, however, clear. Both the models predict a decrease in the vacancy lifetime due to relaxation. This is in the right direction towards explaining the experimental observation<sup>11</sup> of 180 ps. The fact that the jellium model is in better agreement with experiment than the three-dimensional discrete lattice model is less significant. The effect of atomic relaxation on vacancy-trapped-positron lifetime was discussed earlier by Hansen *et al.*<sup>9</sup> These authors had used the degree of relaxation as a parameter to match their calculated lifetime with experiment.<sup>11</sup> Their empirical value of -7% for the first-NN displacement is in good agreement with the

TABLE II. Positron annihilation characteristics in Mo-vacancy clusters using the discrete lattice model. Binding energies here are given with respect to the positron bulk state in Mo.

Void size	Binding energy (eV)	Lifetime (ps)	Annihilation rates		(1/ns) <i>d</i> electrons
			valence	core	
1 (unrelaxed)	3.44	213	2.891	0.387	1.410
1 (relaxed)	2.38	189	3.006	0.532	1.761
9 (unrelaxed)	7.56	320	2.417	0.137	0.572
9 (relaxed)	7.51	323	2.418	0.129	0.555
15 (unrelaxed)	9.17	409	2.199	0.037	0.207

result in Fig. 1. Hautojarvi *et al.*<sup>6</sup> also had studied the positron lifetimes in various voids of Mo earlier using the jellium model. In this calculations, however, they had used 6.0 eV as the positron zero-point energy<sup>19</sup> and 1.2 electrons per Mo atom. We, instead, have used the more recent values<sup>9</sup> of 5.8 eV for the zero-point energy of the positron and 1.0 for the valence electron per atom. These small changes give rise to only minor changes in the calculated lifetimes. Since the present discrete lattice effective medium model for the voids uses the later values,<sup>9</sup> we have repeated the void calculations of Hautojarvi *et al.*<sup>6</sup> so that a direct comparison can be made between two model calculations presented here.

One can further note from Tables I and II that the positron lifetimes rapidly saturate to a fixed value as voids grow. This is in contrast to the results in Fig. 1 where the atomic relaxations appear to have not converged even for the 51-atom void. In relating the atomic relaxations around the 51-atom void to those at surfaces, one should bear in mind that in this paper the atomic relaxations are defined with respect to the unperturbed distance of the atoms measured with respect to the void center. For surfaces, on the other hand, one considers the changes in the interlayer distance due to relaxations.

#### IV. CONCLUSION

In summary, we have carried out total-energy calculations in Mo containing various vacancy clusters. We find that the atomic relaxations around a void oscillate as a function of void size. While the first-nearest-neighbor atoms around a vacancy relax inward, they move outward for larger vacancy clusters. This behavior is governed by electron bonding terms which can be understood qualitatively in terms of a Mo pair-ion potential. The effect of relaxation on monovacancy-trapped-positron lifetime is significant and brings theory to much better agreement with experiment. However, as voids grow, this effect diminishes largely because the positron distribution then becomes more localized. Thus, it is reasonable to use positron annihilation data to estimate atomic relaxations around monovacancies only.

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